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Patent Applicant's Guide - Volume II - National Chapter - US

Annex US.II, page 1

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U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

15675.P291

U.S. APPLICATION NO. (if known, see 37 CFR 1.5)

09/367081

INTERNATIONAL APPLICATION NO.

PCT/FR98/00210

INTERNATIONAL FILING DATE

February 5, 1998

PRIORITY DATE CLAIMED

2/6/97

TITLE OF INVENTION

POROUS COMPOSITE PRODUCT, IN PARTICULAR WITH A HIGH SPECIFIC SURFACE, PREPARATION

APPLICANT(S) FOR DO/EO/US

Jean-Francois Penneau; Francois Capitaine; Philippe Le Goff

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT articles 22 and 39(1).
4. ☐ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☐ A **FIRST** preliminary amendment.
☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
14. ☐ A subsequent specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information:

1 copy of the Preliminary Examination Report with new page 17
1 English translation of the Preliminary Examination Report
1 copy of the Forms PCT/IB/301 & 304

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|---|--|-------------------------------|--|--------------------------|--|
| U.S. APPLICATION NO. (if known, see 37 CFR 1.5) | | INTERNATIONAL APPLICATION NO. | | ATTORNEY'S DOCKET NUMBER | |
| 09/367081 | | PCT/FR98/00210 | | 15675.P291 | |

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|--|--------------|--------------|-------------------|-------------------------------|---------|
| 17. <input type="checkbox"/> The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)): Neither international preliminary examination fee (37 CFR 1.482 nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by EPO or JPO \$970.00 International preliminary examination fee (37CFR1.482)not paid to USPTO but International Search Report prepared by the EPO or JPO. . . . \$840.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee paid to USPTO (37 CFR 1.445(a)(2)) \$760.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$670.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) \$96.00 | | | | CALCULATIONS FOR PTO USE ONLY | |
| ENTER APPROPRIATE BASIC FEE AMOUNT = | | | | \$ | 970.00 |
| Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)). | | | | \$ | |
| CLAIMS | NUMBER FILED | NUMBER EXTRA | RATE | | |
| Total claims | 29 - 20 = | 9 | X \$18.00 | \$ | 162.00 |
| Independent claims | 2 - 3 = | 0 | X \$78.00 | \$ | 0.00 |
| MULTIPLE DEPENDENT CLAIM(S) (if applicable) | | | + \$260.00 | \$ | 260.00 |
| TOTAL OF ABOVE CALCULATIONS = | | | | \$ | 1392.00 |
| Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28). | | | | \$ | |
| SUBTOTAL = | | | | \$ | 1392.00 |
| Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)). | | | | \$ | |
| TOTAL NATIONAL FEE = | | | | \$ | 1392.00 |
| Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property | | | | \$ | |
| TOTAL FEES ENCLOSED = | | | | \$ | 1392.00 |
| \$ | | | | Amount to be: refunded | \$ |
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a. ☒ A check in the amount of \$ 1392.00 to cover the above fees is enclosed.

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A duplicate copy of this sheet is enclosed.

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NOTE: Where an appropriate time limit under 37 CFR 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

Blakely, Sokoloff, Taylor & Zafman LLP
12400 Wilshire Blvd. 7th Floor
Los Angeles, CA 90025-1026

SIGNATURE
 Eric S. Hyman
 NAME
 30,139
 REGISTRATION NUMBER

POROUS COMPOSITE PRODUCT, IN PARTICULAR WITH A HIGH
SPECIFIC SURFACE, PREPARATION PROCESS AND ELECTRODE
FORMED OF A POROUS COMPOSITE FILM FOR AN ELECTRO-

5 CHEMICAL ASSEMBLY

The invention relates to a porous composite product, in particular in the form of a film, in particular with a high specific surface, and to a
10 process for the preparation of such a product.

It also relates to the precursor composite product of use in carrying out the said process.

It also relates to the application of the porous composite product in the form of a film as
15 electrode for the entire range of electrochemical products and to the application in general of the porous composite product, with a high specific surface, in the field of selective membranes, of packaging or of catalysis.

Low density porous films are already known, in particular by Patent Application EP-A-283,187, which are obtained by spinning, at the melting temperature, a mixture of a first thermoplastic polymer and of a second thermoplastic polymer and then removing the
20 second polymer by means of an appropriate solvent. Such a porous film can be used for various applications, in particular in the field of filtration or of separation.

Patent Application EP-A-430,439 discloses a process for improving the production of such films, in
25 which a mixture of a first thermoplastic polymer and of a second immiscible thermoplastic polymer is extruded through a die and then removing the immiscible polymer by means of a solvent, the process being characterized in that a perforated barrier plate is interposed
30 upstream of the die, so as to obtain a porous structure comprising a longitudinal region of low porosity and another longitudinal region of higher porosity.

Furthermore, polarizable electrodes are known which can be used in electrical capacitors of the

double-layer type which are capable of being charged with, or of discharging, a large amount of electric charge.

The polarizable electrodes which can be used in supercapacitors are based on an ideally polarizable material which is light and which has a large exchange surface area, such as active charcoal, which is a carbonaceous material with a high specific surface, in particular greater than $1000 \text{ m}^2/\text{g}$.

For an electrode to exhibit the maximum efficiency, it must have a maximum proportion of active mass and an optimum accessibility to this mass. The latter property requires that it should have an open porous structure. This is the case, for example, with electrodes made of activated fabric: an active charcoal fabric is manufactured from a fabric based on viscose or on polyacrylonitrile, which fabric is carbonized and then activated.

However, such electrodes are expensive and exhibit a high and uneven thickness (generally greater than $300 \text{ }\mu\text{m}$). Furthermore, although such a production method makes it possible, at least in theory, to employ a spooling technology, it turns out in practice that such an operation is difficult to carry out.

Electrodes with a very high proportion of active mass (generally greater than 98%) can also be obtained by sintering. Active charcoal and various additives, in particular conducting black, are mixed mechanically with a liquid until a suspension is obtained. The solution obtained is poured over a filtering partition, which is placed under partial vacuum. After a certain time, all the components are deposited homogeneously on the filtering partition, whereas the liquid has passed through this partition. The partial vacuum creates a degree of cohesion between the components, equivalent to compacting under pressure. The electrode is the dry material recovered on the partition.

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However, as above, this technology exhibits numerous disadvantages. In particular, it lends itself with difficulty to the use of a spooling technology and the thickness, homogeneity and evenness of the electrodes are difficult to control. Furthermore, the processes are limited in the choice of the polymers. In particular, polyolefins cannot be used.

The carbonaceous filler can also be mixed mechanically with a binding polymer in a small proportion, for example 3% of Teflon, until a very viscous paste is obtained, and then rolling in order to give a sheet which is cut up using a hollow punch in order to produce an electrode.

This process results in the same disadvantages as the preceding production methods.

A process for manufacture by coating is also mentioned, in which process the active filler and one or more additives, such as a binding polymer, are mixed with a solvent until a paste of controlled viscosity is obtained. The latter is coated onto a support sheet which can act subsequently as current collector. The sheet passes into an oven in order for the solvent to be evaporated.

The deposit can be relatively thin (down to a few microns) and homogeneous and the proportion of active mass is high.

It is nevertheless a process which is difficult to implement because of the possible use of solvents which can be toxic.

The electrodes in the form of films, in particular of polyolefin films, which make it possible to employ a spooling technology are also known.

These polarizable electrodes are based on a carbonaceous material, for example an active charcoal with a high specific surface, in particular at 1000 m²/g, and on a binder, such as polyolefins, in particular polyethylene or polypropylene, or other polymers, such as polyesters, polycarbonates or polyimides.

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Polarizable electrodes using a polyethylene or polypropylene binder and an active charcoal powder have been provided, for example (JP-A-22062/92).

However, polarizable electrodes based on a
5 binder such as polyethylene or polypropylene exhibit a very low porosity.

Such phenomena also occur with the other binders cited above.

Document BE-A-693,135 discloses porous sheets
10 of polytetrafluoroethylene entirely in the form of fibrils comprising conducting filler materials, such as graphite or a metal, up to 98% of the weight of the sheet.

This type of structure is obtained by mixing an
15 aqueous dispersion of polytetrafluoroethylene particles with an extractable polymer, followed by milling. This milling constitutes a critical stage which results in the shearing of the polytetrafluoroethylene particles and the conversion of the particles into a network of
20 elongated fibers. Extrusion is then carried out and then the extractable polymer is removed. The final structure exhibits pores of greater than 0.1 μm . These sheets can be used as electrode in fuel cells.

The abstract of Japanese document JP-A-57100142
25 discloses the production of a porous membrane which consists in extruding a mixture, by volume, of 15-60% of a polyolefin resin; 3-40% of a polyether; 20 to 80%, by volume, of an extractable, finely divided powder; and 0.5 to 10% of an insoluble powder and in then
30 extracting the polyether and the extractable powder. The Applicant has confirmed that it is impossible by the process disclosed in this document to obtain sheets comprising a higher proportion of filler without seriously affecting the mechanical properties.

35 It would therefore be desirable to produce porous electrodes formed of a binder and of fillers, in particular with a high specific surface, which can be produced in a large amount which make it possible to employ a spooling technology.

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The aim of the present invention is specifically to provide a solution to this technical problem.

- One object of the present invention is to
5 provide novel porous composite products having in particular a high specific surface.

- Another object of the present invention is to provide composite films, in particular with a high specific surface, with a high content of fillers, which
10 make it possible to employ a spooling technology.

Another object of the present invention is to make it possible to use a broad choice of polymers.

- Another object of the present invention is to provide porous composite products or films which are
15 inexpensive to manufacture.

- Another object of the present invention is to make it possible to obtain products of varied shape, because of the extrusion technique used, which can be employed, such as pipes, rods, films or any other
20 extruded object.

Another object of the present invention is to provide carbonaceous electrodes in the form of thin, homogeneous, ideally polarizable porous films which exhibit a very high proportion of active mass.

- Another subject-matter of the present invention relates to the applications of the porous composite products as selective membrane, packaging films or insulating films.
25

- The invention firstly relates to a porous
30 composite product, in particular with a high specific surface, characterized in that it comprises a polymeric material and at least 20% of one or more fillers, in particular with a high specific surface, the said product being capable of being obtained by extrusion.

- The expression "product" is intended to denote an assembly, the cohesion of which is sufficient for it to retain its integrity without being supported.
35

It is significant to note that the products according to the invention exhibit a novel structure

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because of the very high homogeneity of the distribution of the filler, in particular with a high specific surface, in the polymeric material and because of its continuous structure. Furthermore, the polymeric material is non-fibrillated.

This is one of the essential characteristics of the product according to the invention, as the Applicant has observed that a product which does not exhibit a sufficient homogeneity results in inadequate mechanical properties for the level of fillers indicated above.

The expression "capable of being obtained by extrusion" means that the composite product exhibits the characteristics of an extruded product.

In order for the product "capable of being obtained by extrusion" to exhibit the required homogeneity, it is necessary for this extrusion to be carried out on a mixture which is as homogeneous as possible. Such a homogeneous mixture can be obtained from a twin-screw extruder. Other appropriate mixers can also be used.

The products concerned are therefore fundamentally different from those which can be obtained by the coating technique as was described in the preamble of the description.

Preferably, one of the essential characteristics of the porous composite product according to the invention is that it exhibits a high specific surface.

The specific surface is evaluated by the "BET" measurement as described, for example, in the publication Technique de l'ingénieur [Art of the Engineer], Pbis 45-1 (Etude de structure - mesure de surface spécifique) [Structure study - measurement of specific surface), Jean Charpin and Bernard Rasneur.

The specific surface of the porous composite product according to the invention is greater than approximately 10 m²/g and preferably greater than

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20 m²/g. Advantageously, of between 20 m²/g and 100 m²/g.

The porosity of the product is, by volume, greater than 5%. It is generally less than 5 approximately 80%.

For applications in supercapacitors or accumulators, the porosity is generally between 15 and 50%.

This mean diameter of the pores is generally less than 1 μm. According to a preferred alternative form, the mean diameter of the pores is less than 0.5 μm, preferably less than 0.1 μm, advantageously less than 0.02 μm.

In the specific case of fluorinated polyolefins, the diameter of the pores is generally less than 0.5 μm. This is the case in particular with polytetrafluoroethylene.

In addition to the high BET specific surface and the mechanical properties, these products are noteworthy in that the electrochemical capacity is greater than 2 F/g, preferably greater than 10 F/g.

In the case of an electrode for a supercapacitor, the desired porosity is mesoporous, whereas, in the case of Belgian Patent 693,135, which relates to an electrode for "fuel cell" application, the desired porosity must be open (macroporous) in order to allow a high fuel flow.

In the case of porous composite products in the form of films, it should be noted that these films exhibit noteworthy mechanical properties which allow them to be employed by the spooling technology. In general, these films exhibit a tensile strength at break of greater than 4 MPa, advantageous of greater than 6 MPa, at room temperature.

Mention may be made, among fillers, of carbons, such as graphites or carbon blacks with a low specific surface, metal oxides, silica or talcs.

Mention is in particular made, among fillers with a high specific surface which are suitable for the

production of such composite products, of carbonaceous materials or inorganic and metallic particles with a high specific surface, such as, for example, Raney metals, rare earth metal oxides, porous ceramics, or perlites, zeolites or clays.

The properties required for a carbonaceous material are an expanded surface per unit of high weight, a low electrical resistance and good electrochemical stability.

The carbonaceous materials can be provided in the form of powders and are obtained, for example, from oil pitch, phenolic resins, coconut shells and other organic products.

An active charcoal exhibits in particular a specific surface (BET) of between 300 and 3000 m²/g, preferably of greater than 1000 m²/g.

The polymeric material is formed of thermoplastic elastomers or polymers which are insoluble in aqueous and/or organic solvents and which ensure the cohesion of the product (structural polymers or elastomers) and of thermoplastic polymers or elastomers with polar groups which remain in the product after the implementation of the manufacturing process which results in the said porous product or film.

Mention is in particular made, among insoluble elastomers or polymers, of polyolefins, such as polypropylenes, polyethylenes or copolymers of ethylene and of propylene. These polyolefins are such that they can be produced in the form of films and are well known in particular as packaging films. They are, for example, low or high density polyethylene optionally comprising, as copolymer, a greater or lesser proportion of an alpha-olefin.

They may also be polyamides, such as polyether-block-polyamides, polyimides, vinyl copolymers with a high proportion of ethylene monomers, such as poly(ethylene/vinyl acetate) with a high proportion of ethylene monomers, acrylic polymers, aromatic polymers, such as polystyrenes, for example polystyrene-butadiene

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- copolymer, fluorinated polymers, such as poly(vinylidene fluoride), or copolymers formed from monomers belonging to one of the abovementioned families, for example vinylidene fluoride and
- 5 hexafluoropropylene copolymers or vinylidene fluoride and trifluoroethylene copolymers.

The thermoplastic elastomers or polymers which are insoluble in the solvents are preferably chosen from the group of the polyolefins.

- 10 Mention is in particular made, among the soluble polymers, of polymers which are soluble in the following solvents: water, alcohols, dimethylformamide, dimethyl sulfoxide, tetrahydrofuran or acetone.

- With the proviso, of course, that the degree of
- 15 polymerization is appropriate to removal by solvent, the soluble polymers are in particular chosen from polyethers, such as polyoxyethylene or polyoxopropylene, or polyalcohols, such as poly(vinyl alcohol) or ethylene-vinyl alcohol copolymers. Mention is in
- 20 particular made, among these polymers, of those for which the molecular mass is between 200,000 and 1,000,000, advantageously polyethers.

Mention is also made of polymers which can be calcined according to the usual methods.

- 25 The calcinable polymers correspond to the polymers which are soluble in the solvents mentioned above and can also be chosen from polymers with a decomposition temperature below that of the structural polymer or elastomer, for example cellulose.

- 30 The choice of these polymers can be made in a known way by simple tests within the scope of a person skilled in the art.

- The composite product preferably comprises at least 20% by weight of fillers, advantageously between
- 35 30 and 90%, preferably between 50 and 85%.

The composite product preferably comprises 10 to 40% of thermoplastic polymers or elastomers which are insoluble in aqueous and/or organic solvents and 5

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to 40% of polymers which are soluble in aqueous and/or organic solvents.

More preferably, the composite product comprises:

- 5 - 10 to 40% of polyolefin,
- 5 to 40% of polyether,
- fillers, q.s. for 100%.

Another characteristic of the porous composite product according to the invention lies in the fact
10 that it is provided in a homogeneous and even form, that is to say that the fillers are intimately mixed with the polymeric material, unlike, for example, the sheets obtained by coating a mixture of carbonaceous fillers with a small proportion of binding polymer of
15 the polytetrafluoroethylene type.

The composite products according to the invention can be provided in the form of a film and exhibit the advantage of being able to be employed using spooling technology.

20 These films avoid the use of a support.

The invention also relates to a process for the preparation of a composite product as described above, characterized in that:

- 25 a) a mixture comprising one or more insoluble polymers, one or more soluble or calcinable polymers and one or more fillers with a high specific surface is formed,
- b) the said mixture is extruded, so as to form an extruded precursor product,
- 30 c) the soluble or calcinable polymer or polymers is/are removed from the extruded precursor product,
- d) the porous composite product is recovered.

The said process is therefore an extrusion-
35 removal process which makes it possible to obtain a porous composite product with a high specific surface.

The expression "removed" is intended to indicate that a substantial portion of the soluble or calcinable polymers is eliminated in order to form

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pores, it being understood that it is not very probable that these polymers will be completely removed, due in particular to their affinity for the active charcoal.

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In phase a) of the process, all the
5 constituents, namely one or more solvent-insoluble polymers which correspond to the polymeric material forming the structure of the composite product, one or more other solvent-soluble or calcinable polymer or polymers and one or more fillers with a high specific
10 surface, are homogeneously mixed, whether by dissolving or suspending, it being known that the polymers ensuring the cohesion of the composite product (insoluble polymers) and the fillers with a high specific surface are not removed during stage c). The
15 mixing can also be carried out by means of the extruder which allows stage b) to be carried out.

From among the soluble polymers which will be removed during stage c) may be chosen any soluble polymer which can be mixed according to stage a) and
20 mention is in particular made of polymers which are soluble, for example, in water, alcohols, dimethylformamide, dimethyl sulfoxide, tetrahydrofuran or acetone.

With the proviso, of course, that the degree of
25 polymerization is appropriate to removal by solvent, the soluble polymers are chosen in particular from polyethers, such as polyoxyethylene or polyoxypropylene, or polyalcohols, such as poly(vinyl alcohol) or ethylene/vinyl alcohol copolymers.

30 Mention is also made, by way of polymers which can be removed in order to form pores, of polymers which can be calcined according to the usual methods.

The calcinable polymers can be chosen from
35 polymers with a decomposition temperature below that of the structural polymer or elastomer, for example cellulose.

The choice of these polymers can be made in a known way by simple tests within the scope of a person skilled in the art.

The various constituents of the product are mixed at an appropriate temperature, in particular by means of an extruder. In this case, stages a) and b) are carried out simultaneously in order to give an intermediate precursor product exhibiting a very low BET specific surface (less than approximately $1 \text{ m}^2/\text{g}$).

The precursor product can be re-extruded in the form of a film, in particular a thin film with a thickness of less than approximately $300 \text{ }\mu\text{m}$.

- 10 According to an advantageous alternative form, stage b) is therefore carried out in two stages:
- a first extrusion stage (i) consisting in forming granules,
 - a second extrusion stage (ii) consisting in
- 15 forming a film.

The first stage is advantageously carried out in a corotating twin-screw extruder, with a rod die for example, whereas the second stage is advantageously carried out in a single-screw extruder with a flat die.

- 20 The extruded precursor product, either in the form of granules or in the form of films, is subsequently subjected to the removal stage c) in which the soluble polymer is eliminated.

- This removal stage can be carried out in particular by dissolving the soluble polymer by bringing it into contact with an appropriate solvent.

- A calcination can also be carried out according to a known process which consists in slowly raising the temperature up to the decomposition temperature of the polymer to be removed.

The products are subsequently recovered and exhibit a "BET" specific surface of greater than approximately $10 \text{ m}^2/\text{g}$, preferably of greater than approximately $20 \text{ m}^2/\text{g}$.

- 35 Another subject-matter of the invention is therefore the porous composite products with a high specific surface formed of a polymeric material and of one or more fillers with a high specific surface, characterized in that they are capable of being

obtained by the extrusion-removal process as described above.

Another subject-matter of the present invention is the precursor products obtained before the removal stage, these precursor products, of use in particular in carrying out the process described above, comprise one or more solvent-insoluble polymers, one or more other solvent-soluble or calcinable polymers and one or more fillers with a high specific surface.

The insoluble polymers/soluble or calcinable polymers ratio by weight is preferably between 0.1 and 5, advantageous 0.1 and 2.

The proportion of fillers with a high specific surface in the solvent-free mixture leading to the precursor product is preferably between 20 and 60% by weight.

The invention also relates to an electrode in the form of a film, which electrode is formed of a porous composite product with a high specific surface according to the invention.

These electrodes in the form of porous films can generally be used for the production of electrochemical assemblies, such as accumulators, double-layer capacitors or supercapacitors.

The supercapacitors are formed in a known way of two polarizable electrodes and of a separator impregnated with an electrolyte. These assemblies are also denoted by the term "electrolytic double-layer capacitor".

The electrodes according to the invention greatly improve the capacity of the films, in particular by the very high proportion of active mass which can be obtained.

Particular mention is made of the following fields of applications:

- Porous electrodes for the electrochemical storage of energy [electrochemical generators, redox accumulators, air accumulators, electrochemical supercapacitors or double-layer capacitors, or fuel cells].

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- Porous electrodes for electrodialysis processes [production of drinking water, production of salt from sea water, demineralization of organic products (wheys, milk, wine, and the like),
5 desalination of water for consumption, softening of boiler water or decontamination of nuclear power station effluents].

- Porous electrodes for capacitive deionization processes [production of drinking water, production of
10 salt from sea water, demineralization of organic products (wheys, milk, wine, and the like), desalination of water for consumption, softening of boiler water or decontamination of nuclear power station effluents].

15 - Porous electrodes for electrolysis processes [production of chlorine and sodium hydroxide, electrolysis of water or production of acid and a base from a salt].

20 - Electromembranes for dialysis and electro-dialysis processes [production of drinking water, production of salt from sea water, demineralization of organic products (wheys, milk, wine, and the like), desalination of water for consumption, softening of boiler water or decontamination of nuclear power
25 station effluents].

- Electromembranes for filtration processes [selective electrofiltration of organic products or microfiltration].

30 The invention also relates to the application of these composite products in the form of granules or films:

- to methods for filtration and for adsorption, for example dehumidification of gaseous or liquid surroundings, selective adsorption
35 (physical and/or chemical), molecular sieves or filtration of polluted air,
- to catalysis,
- to energy exchanges (for example, thermal or sound insulation or heat exchangers),

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- to packaging, in particular the packaging of delicate products requiring selective permeability.

The invention is now illustrated by the following examples, given by way of indication:

Example 1:

The proportions by mass of the starting compounds (powders) are as follows:

- 40% active charcoal (with a specific surface of 1250 m²/g)
- 20% ethylene-propylene copolymer
- 40% polyoxyethylene (POE 300,000).

The combined powdered constituents are mixed as homogeneously as possible by mixing by means of a corotating twin-screw extruder with a length of 40D and with two kneading regions and three transportation regions. The device used is a twin-screw with a diameter of 58 mm and the temperature profile used is as follows:

50/120/120/110/110/100/100/120/120/150/170.

Die pressure: 8 MPa

Number of revolutions per minute: 85

Throughput: 34 kg/h.

The granules obtained are introduced into a single-screw with a length of 30D for extrusion of a primary mixture. The device used is a twin-screw with a diameter of 30 mm and the temperature profile used is as follows:

165/170/170/170/185°C.

Die pressure: 8 MPa

Number of revolutions per minute: 10

Throughput: 2 kg/h.

The film obtained has a thickness of 200 μm.

The following stage consists in immersing the film obtained in water at room temperature for a residence time of 5 minutes. The film is then dried at 40°C for 1 hour.

The mean proportions by mass of the compounds after treatment are as follows:

- 52% active charcoal
- 26% ethylene-propylene copolymer
- 22% polyoxyethylene.

It is possible to metallize with aluminum (for
5 example: 0.5 Ω/\square the films obtained, before or after
treatment, in a metallizing device at a pressure of the
order of 0.01 Pa (10⁻⁴ mbar).

The physical characterization of the films
obtained, metallized or otherwise, results in the
10 following data:

- elongation at break (see table below)
- spooling tension (core with a diameter of
6 mm): 0.05 g/ μ m/mm
- electrochemical capacity of 26 F/g of
15 electrode (measured via the slope of the discharge
curve of the supercapacitor, in galvanostatic mode)
- "BET" specific surface of less than 1 m²/g of
film at the outlet of the extrusion and "BET" specific
surface of 28 m²/g of film after passing into water
20 according to the method which consists in immersing the
electrode for approximately five minutes.

Example 2

The proportions by mass of the starting
25 compounds (powders) are as follows:

- 40% active charcoal (with a specific surface
of 1250 m²/g)
- 10% ethylene-propylene copolymer
- 50% polyoxyethylene (POE 300,000).

30 The combined powdered constituents are mixed as
homogeneously as possible by mixing by means of a
corotating twin-screw extruder with a length of 25D and
with two kneading regions and three transportation
regions. The device used is a twin-screw with a
35 diameter of 19 mm and the temperature profile used is
as follows: 160/170/180/190/200°C

Die pressure: 10.5 MPa

Number of revolutions per minute: 400

Throughput: 1.8 kg/h.

The granules obtained are introduced into a single-screw with a length of 30D for extrusion of a primary mixture. The device used is a twin-screw with a diameter of 30 mm and the temperature profile used is as follows: 160/170/180/190/220°C.

Die pressure: 17.5 MPa

Number of revolutions per minute: 15

Throughput: 2.5 kg/h. The film obtained has a thickness of 180 μm .

The next stage consists in immersing the film obtained in water at room temperature for a residence time of 5 minutes. The film is then dried at 40°C for 1 hour.

The mean proportions by mass of the compounds after treatment are as follows:

- 60% active charcoal
- 15% ethylene-propylene copolymer
- 25% polyoxyethylene.

It is then possible to metallize with aluminum (for example: 0.5 Ω/\square the films obtained in a metallizing device at a pressure of the order of 0.01 Pa (10^{-4} mbar).

The physical characterization of the films obtained, metallized or otherwise, results in the following data:

- elongation at break (see table below)
- spooling tension (core with a diameter of 6 mm): 0.05g/ $\mu\text{m}/\text{mm}$
- electrochemical capacity of 26 F/g of electrode according to the method described in Example 1
- "BET" specific surface of less than 1 m^2/g of film at the outlet of the extrusion and "BET" specific surface of 60 m^2/g of film after passing into water according to the method described in Example 1.

Mechanical characterization measurement of
the films obtained

| Temperature | Film | Elongation at break (%) | Modulus of elasticity (Dn/mm ²) | Force (Mpa) |
|-------------|-----------|-------------------------------|---|----------------|
| 20°C | Example 1 | 0.97 | 134 | 8.3 |
| 20°C | Example 2 | 0.89 | 170 | 9.3 |
| 40°C | Example 1 | 1.14 | 88 | 6.1 |
| 40°C | Example 2 | 1.20 | 125 | 7.2 |
| 60°C | Example 1 | 5.73 | 22 | 2.0 |
| 60°C | Example 2 | 1.68 | 30 | 2.6 |

5 Example 3

The proportions by mass of the starting compounds (powders) are as follows:

- 40% active charcoal (active charcoal with a specific surface of 1250 m²/g)
- 10 - 20% ethylene-propylene copolymer
- 40% polyoxyethylene (POE 300,000).

The combined powdered constituents are mixed as homogeneously as possible by mixing by means of a corotating twin-screw extruder with a length of 40D and
15 with two kneading regions and three transportation regions. The device used is a twin-screw with a diameter of 58 mm and the temperature profile used is as follows:

50/120/120/110/110/100/100/120/120/150/170.

20 Die pressure: 8 MPa

Number of revolutions per minute: 85

Throughput: 34 kg/h.

The next stage consists in immersing the granules obtained (2 mm/² mm) in water at room
25 temperature for a residence time of 5 minutes. The film is then dried at 40°C for 1 hour.

The mean proportions by mass of the compounds after treatment are as follows:

- 60% active charcoal
- 30 - 15% ethylene-propylene copolymer

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- 25% polyoxyethylene.

The granules obtained exhibit an expanded surface of 30 m²/g.

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CLAIMS

1. Porous composite product, characterized in that
5 it is formed of a polymeric material and at least 20%
of one or more fillers and in that the said product is
capable of being obtained by extrusion.
2. Porous composite product according to Claim 1,
characterized in that it exhibits a high specific
10 surface.
3. Composite product according to Claim 1 or 2,
characterized in that the mean diameter of the pores is
less than 0.5 μm .
4. Composite product according to Claim 1,
15 characterized in that the polymeric material comprises
elastomers or polymers chosen from the group consisting
of polyolefins, which are optionally fluorinated,
acrylic polymers, aromatic polymers, polyamides,
polyimides, vinyl polymers with a high proportion of
20 ethyl monomers and optionally thermoplastic polymers or
elastomers, soluble in polar organic solvents or water,
which remain after the implementation of the
manufacturing process.
5. Composite product according to Claim 4,
25 characterized in that the polymeric material comprises
elastomers or polymers chosen from the group consisting
of polyethylenes, polypropylenes, ethylene- α -olefin
copolymers and optionally thermoplastic polymers or
elastomers, soluble in polar organic solvents or water,
30 which remain after the implementation of the
manufacturing process.
6. Composite product according to either of
Claims 4 and 5, characterized in that the thermoplastic
elastomers, soluble in polar organic solvents or water,
35 which remain after the implementation of the
manufacturing process are chosen from polyethers,
poly(vinyl alcohol)s or ethylene-vinyl alcohol
copolymers, preferably polyethers with a molecular mass
of between 200,000 and 1,000,000.

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7. Composite product according to Claim 6, characterized in that the composite product comprises:
- 10 to 40% of polyolefin,
 - 5 to 40% of polyether,
 - fillers, q.s. for 100%.
8. Composite product according to Claim 1, characterized in that the filler is chosen from fillers with a high specific surface, composed in particular of active charcoal, inorganic particles or metallic particles.
9. Composite product according to Claim 8, characterized in that the filler exhibits a specific surface of between 300 and 3000 m²/g.
10. Composite product according to one of the preceding claims, characterized in that it comprises between 30% and 90% by weight of filler.
11. Composite product according to Claim 10, characterized in that it comprises 50 to 85% by weight of filler.
12. Composite product according to one of the preceding claims, characterized in that it exhibits a "BET" specific surface of greater than 10 m²/g, preferably of greater than 20 m²/g.
13. Composite product according to one of the preceding claims, characterized in that it is provided in the form of a film.
14. Composite product according to Claim 13, characterized in that the product in the form of a film exhibits a tensile strength at break of greater than 4 Mpa, preferably of greater than 6 MPa.
15. Composite product according to one of Claims 1 to 12, characterized in that it is provided in the form of granules.
16. Process for the preparation of a porous composite product according to one of Claims 1 to 15, characterized in that: -
- a) a homogeneous mixture comprising one or more insoluble polymers, one or more soluble or

calcinable polymers and one or more fillers, in particular with a high specific surface, is formed,

b) the said mixture is extruded, so as to form an extruded precursor product,

- 5 c) the soluble or calcinable polymer or polymers is/are removed from the extruded precursor product, in order to form pores,

d) the porous composite product is recovered.

- 10 17. Preparation process according to Claim 16, characterized in that the removal of stage c) is carried out by bringing the extruded precursor product into contact with an appropriate solvent.

- 15 18. Preparation process according to Claim 17, characterized in that the removal of stage c) is carried out by subjecting the extruded precursor product to a calcination.

19. Preparation process according to Claim 16, characterized in that stage a) is carried out by means
20 of a mixer or of a twin-screw extruder, ensuring homogeneous mixing of the polymers and of the fillers, in particular with a high specific surface.

20. Preparation process according to one of Claims 16 to 19, characterized in that the insoluble
25 polymer/soluble or calcinable polymer ratio by weight is between 0.1 and 5.

21. Extruded composite precursor product of use in particular in carrying out the process according to one of Claims 16 to 19, comprising one or more insoluble
30 polymers, one or more other soluble or calcinable polymers and one or more fillers, in particular with a high specific surface.

22. Electrode for an electrochemical assembly, such as an electrochemical generator or accumulator,
35 characterized in that it is formed of a film of porous composite product according to Claim 13 or 14 with an electrochemical capacity of greater than 2 F/g, preferably of greater than 10 F/g, and of an electrochemically active material.

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23. Electrode for a supercapacitor or capacitor, characterized in that it is formed of a film of porous composite product according to Claim 13 or 14, characterized in that the electrochemical capacity is
5 greater than 2 F/g, preferably greater than 10 F/g.

24. Electrochemical assembly, in particular an electrochemical generator, capacitor or supercapacitor comprising two electrodes according to Claim 22 or 23 and a separator impregnated with an electrolyte.

10 25. Application of the composite products according to either of Claims 13 and 14 for the electrochemical storage of energy.

26. Application of the composite products according to either of Claims 13 and 14 for packaging or
15 insulation.

27. Application of the composite products according to one of Claims 1 to 12 and 15 for selective filtration.

28. Application of the composite products according to either of Claims 13 and 14 for electrodialysis or
20 capacitive deionization processes.

29. Application of the composite products according to either of Claims 13 and 14 for the electrolysis process.

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DECLARATION AND POWER OF ATTORNEY FOR PATENT APPLICATION

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below, next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

POROUS COMPOSITE PRODUCT, IN PARTICULAR WITH A HIGH SPECIFIC SURFACE, PREPARATION PROCESS AND ELECTRODE FORMED OF A POROUS COMPOSITE FILM FOR AN ELECTROCHEMICAL ASSEMBLY

the specification of which

is attached hereto
 X was filed on February 5, 1998
 Application Serial No. PCT/FR98/00210 as
 And was amended on
 (if applicable)

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above. I do not know and do not believe that the same was ever known or used in the United States of America before my invention thereof, or patented or described in any printed publication in any country before my invention thereof or more than one year prior to this application, that the same was not in public use or on sale in the United States of America more than one year prior to this application, and that the invention has not been patented or made the subject of an inventor's certificate issued before the date of this application in any country foreign to the United States of America on an application filed by me or my legal representatives or assigns more than twelve months prior to this application.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, Section 1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, Section 199, of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor(s) certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)**Priority Claimed**

| | | | | |
|-----------------------------|----------------------------|---|-------------------|----|
| 97 01350 (Number) | FRANCE (Country) | 06/February/1997 (Day/Month/Year Filed) | Yes Yes | No |
| (Number) | (Country) | (Day/Month/Year Filed) | Yes | No |
| (Number) | (Country) | (Day/Month/Year Filed) | Yes | No |

I hereby claim the benefit under Title 35, United States Code, Section 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, Section 112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, Section 1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application.

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PCT/FR98/00210
(Application Serial No.)

05/February/1998
(Filing Date)

Pending
(Status - patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status - patented, pending, abandoned)

(Application Serial No.)

(Filing Date)


(Status - patented, pending, abandoned)

I hereby appoint BLAKELY, SOKOLOFF, TAYLOR & ZAFMAN, a firm including :

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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Date: January 11, 2000

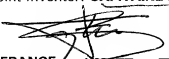
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